

**Answer to second reviewer  
(the reviewer's comments are in italic).**

*General Comments:*

*This manuscript presents an interesting study of the water chemistry of a unique hyperalkaline hydrothermal system in the Prony Bay of New Caledonia. This system is an exciting example of alkaline fluids produced by serpentinisation reactions with meteoric water in ultramafic rocks that in turn react with coastal seawater to form spectacular brucite-carbonate structures at different sites in the Prony Bay. This is the first example of such a system that forms at a marine-terrestrial interface. Similar alkaline systems associated with the alteration of ultramafic rocks have been found at the Lost City hydrothermal field near the Mid-Atlantic Ridge (pure marine, ridge system) and in the Mariana forearc (marine, subduction setting) as well as at a number of continental sites (pure meteoric systems), such as in California, Oman, N. Italy, Bosnia, and Turkey.*

*Such systems have received increased attention in the past few decades because of the associated high concentrations of hydrogen and methane that can sustain diverse microbial communities in environments with limited CO<sub>2</sub> and nutrients and which may be analogous to early Earth environments or conditions on other planets. Thus, the Prony Bay system is of general interest to a wide range of Earth scientists.*

*This study is part of a larger sampling and analyses campaign resulting from the HYDROPRONY cruise which took place at the end of 2011. The authors indicate that they will present and discuss the gas data in a separate paper. Although not mentioned specifically, one assumes that the mineralogical data and geomicrobiological studies will also be forthcoming.*

A first microbiological study is now in press (Quemeneur et al., *Env. Microbiol. Reports*). A second one (Postec et al.,) is about to be submitted to PLOS One.

The mineralogical and geobiological data are also the subject of a separate study that is being finalized (Pisapia et al., *PNAS*, in prep., to be submitted during the summer 2014). Some of these results have been presented at conferences such as the Goldschmidt Conference in Florence (Italy) in 2013. The abstract (Pisapia et al., 2013) is available in the *Mineralogical Magazine*. An overall description of the mineralogy and chemistry of the concretions of the Prony vents is also in preparation.

*This study focuses on the chemistry of the major elements at 6 sites of high pH discharge, which show large variations in pH, salinity and dissolved components as a result of variations in the degree of mixing with coastal seawater. The authors then calculate mineral saturations to constrain the conditions of brucite and carbonate formation in this distinct alkaline environment. A clear discussion of the link between fluid chemistry and microbiology is not given, and hence one may question its impact from publication in *Biogeosciences*.*

*Specific Comments:*

*The data and calculations made in this study are a valuable contribution to a better understanding of the controls on alkaline fluid compositions associated with the alteration of*

*ultramafic rocks at low temperatures. The presentation and the discussion of the chemistry of the major constituents of the hydrothermal fluids are straightforward and provide a good example of the influence of mixing of two (or three) distinct fluids and changes associated with mineral precipitation.*

*The discussion of the chemical data concentrates primarily on the controls on the variations in pH, Mg, Na and Cl at the different sites – i.e, mixing and Mg-Ca mineral precipitation. It would have been nice to see a more detailed discussion of the DIC and sulfate data and the implications of these, as well as the volatiles, for microbial activity. Since this manuscript is intended for Biogeosciences, a discussion of the relevance of the study for microbiology would make it more attractive.*

We agree with reviewer that the inclusion of a discussion of microbiology would fit into a manuscript for Biogeosciences. So we propose to include the following paragraph in page 6244, after the sentence " Indeed gases emitted at the alkaline springs of the Prony bay are enriched in H<sub>2</sub> and CH<sub>4</sub>. They serve as important energy and carbon sources for microorganisms that thrive in the porous chimney walls.":

"Various degree of mixing of the anoxic alkaline fluid at with oxygenated ambient seawater also provides potential electrons acceptors (such as sulfates, nitrates or oxygen) crucial for many microbial metabolisms. This was recently evidenced by molecular survey conducted on Prony chimneys (Quémeneur et al., 2014) showing the dominance of the microbial metabolic groups using either of H<sub>2</sub> or CH<sub>4</sub> as electron donors for growth either under the anaerobic conditions such those found in the anoxic parts of the porous structure bathed by the less diluted fluid; It concerns notably Methanosarcinales a group of archaea including both hydrogenotrophic methanogens and members responsible for the anaerobic oxydation of methane, a reaction thermodynamically unfavorable unless coupled with sulfate or nitrate reduction via syntrophic association (consortia) with sulfate or nitrates reducing bacteria (Knittel and Boetius, 2009). Remarkably these Methanosarcinales in Prony are very similar to those previously detected in Lost City chimneys (Brazelton et al., 2006; Schrenk et al., 2004) and in the Prony ecosystem, sulfate-reducing bacteria of the delta-proteobacteria are also well represented (Quémeneur et al., 2014) as noticed in Lost City (Brazelton et al., 2006). Aerobic respirations of hydrogen or methane (and other C1 compounds) are also most likely presents in Prony chimney as strongly suggested by the abundance of sequences related to hydrogenotrophic bacteria of the Burkholderia class, such as Hydrogenophaga and many taxa representing methylotrophic bacteria (Quémeneur et al., 2014). "

Brazelton, W. J., Schrenk, M. O., Kelley, D. S., and Baross, J. A., 2006, Methane- and sulfur-metabolizing microbial communities dominate the Lost City hydrothermal field ecosystem: Appl Environ Microbiol, v. 72, no. 9, p. 6257-6270.

Knittel, K., and Boetius, A., 2009, Anaerobic oxidation of methane: progress with an unknown process: Annu Rev Microbiol, v. 63, p. 311-334.

Schrenk, M. O., Kelley, D. S., Bolton, S. A., and Baross, J. A., 2004, Low archaeal diversity linked to subseafloor geochemical processes at the Lost City Hydrothermal Field, Mid-Atlantic Ridge: Environ Microbiol, v. 6, no. 10, p. 1086-1095.

*In addition, a discussion of the mineral reactions in the ultramafic rocks (serpentinisation processes) that lead to the alkaline compositions and particularly to the “Ca-OH-type” fluids was missing.*

We do not think it is necessary to include in our paper the chemical reactions describing the complex serpentinization process. This can be found in various forms in many papers, including one of ours (Chavagnac et al., 2013b).

About the "Ca-OH water type", we wrote in our answer to the first review: "We think that the term is rather explicit. Is it necessary to add a sentence saying that a Ca-OH water is a water where Ca and OH are the dominant ions?"

*Although there is a slight increase in temperature of the outflow fluids compared to ambient conditions, it is questionable if the term “hydrothermal” is truly appropriate for this system.*

There have been extended discussions within the scientific community about the term "hydrothermal". One can refer to the following paper (Machel, H.G., Lonnee, J., 2002. Hydrothermal dolomite—a product of poor definition and imagination. *Sediment. Geol.* 152, 163-171) where it can be read in the abstract that "we suggest to use White's [Geol. Soc. Amer. Bull. 68 (1957) 1637] time-honored definition of “hydrothermal” as “aqueous solutions that are warm or hot relative to its surrounding environment”, with no genetic implications regarding the fluid source".

This point of detail needs not be discussed in our paper: the Prony Bay system is truly hydrothermal.

*Paper Title: Because the paper essentially focuses on the fluid compositions and does not truly give an overview of the alteration processes, I would suggest changing the title to emphasise the fluid chemistry and importance of serpentinisation processes, for example: “Fluid chemistry of the low temperature hyperalkaline hydrothermal system of the Prony Bay (New Caledonia).*

*Note: “Prony Bay” is a proper name, and “Bay” should be capitalised throughout the text.*

Agreed. We changed the title.

*Introduction: the Lost City hydrothermal system is NOT an example of weathering of ultramafic rocks. It is, however, an example of a hydrothermal system controlled by serpentinisation processes (at T 100-150\_C) in a marine environment. If the Prony Bay fluids are controlled by weathering processes (a process that is different than hydrothermal reactions at elevated temperature), then this should be discussed in more detail in the paper.*

We changed the word "weathering" for "alteration" in the introduction (line 22 page 6224) taking into account that in its general use "weathering" relates to a surficial process.

*Figures: The size of the figures, the symbols and labels in Figures 5, 6, 7 and 10 are too small to be useful for any printed version of the manuscript (and need to be magnified greatly in a PDF version). It would be nice to re-draw these in a larger format.*

We wait for instructions from the editor.

*Was the composition of “standard seawater” measured in the Prony Bay?*

No, we took the composition of standard seawater in Millero's book. We added the reference in the caption of Figure 7.

*Were any analyses made of rain or river water that feed this system?*

No, unfortunately. The characterization of the hydrologic regime of southern New Caledonia is a highly desirable goal and a major undertaking well outside the scope of the present paper. As we state in page 6232, for now we have installed temperature recorders at several locations in the Prony bay in a first attempt to monitor the dynamics of the hydrothermal system and its response to hydrologic conditions (rainfall patterns in a tropical climate). Beyond this remark is the question of the geometry of the hydrothermal system and of the residence time of the waters: where are the recharge zones? Are there other underwater springs outside the Prony Bay further south in the Southern lagoon? Is there any freshwater discharge beyond the coral barrier?

*It would be good to include at least the seawater end-member composition in Table 2.*

Agreed. This will be included in the revised manuscript

*Technical and typographical corrections:*

*Abstract: Page 6223, line 7: change “have been collected” to: were collected*

Done

*Introduction: P. 6224, L. 22: see comment above about using the term “weathering” P.*

See our answer above.

*6225, L. 20: The use of the word “present” is incorrect here. Use “have” instead.*

Done

*P. 6226, L. 4: change “have been collected” to: were collected*

Done

*Section 3.2: P. 6230, L. 25: change “details” to “detail” P. 6231, L. 10: Replace “associated to” with “and”. NB: in English, something is associated with, not associate to. . .*

*Section 4.1: P. 6232, L. 1: Delate “has” – i.e., Garnier (1981) measured. . .*

*Section 4.2: P. 6232, L. 16: Gas bubbles WERE observed – not “have been”..*

*P. 6232, L. 8: Change to: During the fall 2012, we installed temperature recorders*

*P. 6232, L. 22: replace “that at” with “than at”*

These remarks have been taken into account.

*Section 4.4: P. 6234, L. 9: UNCLEAR what is meant by “merely contain anything but calcium and hydroxide” – same problem again on Page 6240, Line 11. Please reformulate the sentence to make it clear what you mean.*

We reworded the sentence to "the freshest samples are the two samples taken at the Kaoris spring for which calcium and hydroxide are the dominant aqueous compounds, all other solutes exhibiting trace concentrations".

*P. 6234, L. 20: replace “for” with “from”*

Done

*P. 6234, L. 27: UNCLEAR what is meant with “limitation”. Do you mean: the upper limit of pH in low temperature serpentinising environments remains an open question? Or something like that?*

Yes this is what we meant. We thus changed the sentence to " the question of the upper pH limit in low temperature serpentinizing environments...".

*P. 6235, L. 12: delete “comprised”*

*P. 6236, L. 25: change “allow taking into account” to allow us to take into account*

*P. 6237, L. 6: what is “prenset” typo for “present”?*

Yes it is a typo. All these remarks have been taken into account.

*Section 5.2 Reformulate paragraph in Lines 13-16. Not proper English.*

We propose the following formulation: "All forms of silica are undersaturated over the whole pH range. This is the case for marine waters (low pH) and for very alkaline waters in which silica becomes very soluble (see the example of Oman and Liguria in Chavagnac et al., 2013b).".

*Section 6: Change Discussion and conclusions . . . (i.e., plural) P. 6241,*

*L. 17: change “has been” to “was”*

*P. 6241, L. 23: Poorly formulated: The tide effects are not sensitive. . .”*

We changed the sentence to "The tide effects are very attenuated at the end of the Baie du Carenage...".

*P. 6241, L. 29: Change “evidenced by” to “indicated by”*

Done